Electrochemical Synthesis of Borides and Silicides of Chromium, Molybdenum and Tungsten in Molten Salts

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Keywords: molten salts, borides, silicides, chromium, molybdenum, tungsten

On the basis of thermodynamic analysis of chemical and electrochemical reactions possible systems and conditions have been determined for the electrolysis of boride and silicides of chromium, molybdenum and tungsten in molten salts. Electrolysis of chromium, molybdenum, tungsten and boride and silicidel powders was realized under kinetic conditions.

Keywords: molten salts, borides, silicides, chromium, molybdenum, tungsten

Samsonov G.V., et al. [1,2] make an comparative analysis of existing methods for obtaining chromium, molybdenum, tungsten silicide and boride, and has shown that one of the most promising methods is electrochemical synthesis in molten salts (ESMS), which was used also for borides high temperature electrodepositions [3,4]; Novoselova I.A., et al. [5], described theoretical backgrounds for different classes of compounds, including carbides, silicides, borides, sulphides, and intermetallics and Malyshev VV, et al. [6,7] the possibility of ESMS on the surface of the semiconducting and dielectric materials was shown. Detailed descriptions were published of the theoretical foundations and practical implementation of the synthesis of tungsten carbide [8,9] and Mo [10]. First electrochemical synthesis of silicides was carried out by French explorer Dodero M. [apud 11,12]. Silicides of titanium, zirconium, and chromium were synthesized by him through electrolysis of molten mixtures of K,SiF 4 and Na,SiF 4, with oxides and fluorides of titanium, zirconium, and chromium. Delimarskii Yu.K. et al. [13] have synthesized TiSi 2 by electrolysis of molten NaCl-KCl-K 2SiF 6 system. An attempt was made [13] to study the cathode processes during the deposition of TiSi 2 from chlorine-fluoride melts. In the US, patent [14] was issued for the electrodeposition of coatings on various products surface is known [25] This method requires using the melt of the following composition, wt.

Later on, the electrolysis of borides was developed in three areas [18]:
- electrolysis from oxide melts;
- electrolysis from halide melts;
- electrolysis from mixed oxide-halide melts.

Oxide melts (molten alkali borates (preferably LiBO 2 and NaBO 2)) and alkaline earth borates, to which titanium compounds are added (TiO 2, Li 2TiO 3, Na 2TiO 3), were used by the authors [19-22] for obtaining of titanium boride coatings on conductive substrates (Ni, Mo, stainless steel etc.). As the anode, Ti or sintered TiB 2 were used; temperature was 1123-1223 K; cathodic current density i was 0.04-0.4 A·cm -2; coating growth rate was between 22 and 220 microns per hour. The anode made of TiB 2 ensures the stability of the bath composition.

In the US, patent was issued in 1960 [23] for electrodeposition of titanium and zirconium diborides (this method can also be applied for other borides) from fluoride-chloride melt NaCl-KCl-K 2TiF 6(K 2ZrF 6)-KBF 4. In [24], other method for the obtaining of coatings by cathodic deposition of TiB 2 in salt melt; to which BF 3 ions are introduced through gaseous BF 3 dissolution, with soluble titanium anode and pure boron anode. Melt must necessarily contain an alkali metal fluoride; the BF 3 ions concentration in it should be 20.0 wt.% and the concentration of titanium ions: 0.5-4.0 wt.%. Besides the indicated components, additives of fluorides of Mg, Ba, Ca, Sr etc. can be added to the melt. Coatings deposition temperature was 810-1033 K, and cathodic current density (i), was 10-500 mA·cm -2.

A method for the preparation of titanium diboride coating on various products surface is known [25] This method requires using the melt of the following composition, wt.

In [26], tantalum boride electrolysiss from fluoride-chloride melt KCl-K 2TaF 7-KBF 4 was described. By varying the composition of the electrolyte, the anode voltage, and current applied to the bath, either a mixture of tantalum mono- and diboride or one of these borides was obtained.
For mixed halide-oxide systems, method of producing TiB₂ and ZrB₂ in molten sodium salts [27] should be noted. To obtain TiB₂ at 1273 K with the current density 150 A dm⁻² electrolysise should be carried out in the melt of the following composition, wt. %: TiO₂:3.0, Na₂CO₃:4.0, Na₂AlF₆:20.0, Na₂B₄O₇:20.0, NaCl:45.0. For zirconium diboride obtaining electrolysise was carried out at 1298 K with current density 120-240 A dm⁻² in the melt of the following composition, wt. %: ZrSiO₄:12.0, NaOH:4.0, Na₂AlF₆:40.0, Na₂B₄O₇:20.0, NaCl:20.0, NaF:4.0.

In [28], the electrolytic production of diborides from oxides is described. For TiB₂, ZrB₂, and HfB₂ obtaining, corresponding melts were used based on Na₂Cl-Na₂AlF₆, Na₂B₄O₇(NaOH) containing TiO₂, ZrO₂, and HfO₂, respectively. Electrolysise temperature was 1323 K, and the current density was 150 A dm⁻².

A process is known [29] for preparation of zirconium diboride at 1023 K with the cathode current densities within the 5-100 mA cm⁻² range from the fluoride-oxide melt of the following composition, wt. %: FLINAK (Li, Na, K)/KF:80.0, K₂ZrF₄:10.0, B₂O₃:10.0. Instead of K₂ZrF₄, zirconium tetrafluoride ZrF₄ can be used. Zirconium diboride was also obtained from ZrO₂ and B₂O₃ dissolved in equimolar K₂ZrF₄-KBF₄ at 873 K [30]. The process is controlled by the concentration of B₂O₃ in the melt, and, at high current densities, zirconium is coprecipitated.

Aleond [31] has used the method of Marion to obtain other compounds. He was also able to synthesize the molybdenum and tungsten diborides. For this purpose, molten KF-KBF₄-WO₃(MoO₃) system was used. Varying amounts of oxides of molybdenum and tungsten, Aleond has synthesized borides W₂B₅, WB, Mo₂B₅, and MoB.

Among the works carried out recently, high-temperature synthesis of dispersed powders of borides of vanadium [32], niobium [33], and tantalum [34] from halide melts should be noted. Of particular interest are articles [35, 36] concerning the synthesis of dispersed powders of titanium and zirconium borides. According to the authors of these articles, in the latter case, discharge of heteronuclear complexes of titanium (zirconium) and boron occurs at the cathode.

Thus, analysis of the current state of the problem of IMES of silicides and borides shows that the further development of the method is possible only on the basis of clarifying the mechanism of, and of the development of principles for the implementation and management of, multi-electron electrode reactions of electrodeposition of chromium, molybdenum, tungsten, silicon, and boron. As a prerequisite for the electrodeposition of compounds is, according to [5], the proximity of potentials of deposition of components, it is necessary to develop ways to bring them together and to find the conditions for the alignment of the potentials of various components deposition processes.

**Experimental part**

Cyclic voltammetry studies were carried out with a TACUSSELL potentiostat PRT 20-10X connected to a PC for data acquisition and control. The electrochemical cell design was described in figure 1.

A platinum wire immersed in the melt was a quasi-reference electrode (QRE). Graphite MPG-7 crucibles served as container for the melt; the same sort of graphite was anode.

Electrolysise with nickel or tungsten bars as cathode were also performed. The powdered product from the working cathode was separated mechanically and crushed.

Results and discussions

**Thermodynamic backgrounds of ESMS**

Equilibrium potentials of compounds decomposition were calculated from the standard Gibbs free energy for the decomposition reaction:

\[ E_p = -\frac{\Delta G^o}{nF} \tag{1} \]

where \( \Delta G^o \) is the standard free energy of the decomposition reaction of the compound to the corresponding components at the temperature T, n-the number of electrons involved in the redox reaction; F-Faraday number.

In calculations, thermodynamic values were used from references [37,38]. During electoreduction of silicon and boron compounds at the cathode, as in the case of carbonates [8,10], several cathode processes occurrence are possible:

1) formation of elementary silicon and boron from oxide and fluoride containing ions

\[ \text{BO}_2 + 3e^- + H_2O \rightarrow \text{B}_4\text{O}_7^{4-} + 2\text{H}^+ \tag{2} \]

2) alkali metal deposition

\[ M^+ + e^- \rightarrow M \tag{8} \]

At the anode, the following reactions can occur:

\[ \text{B}_2\text{O}_3 + \text{BO}_2^{2-} + 0.5\text{H}_2\text{O} \rightarrow 2\text{BO}_2^{4-} + 2e^- \tag{9} \]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{B}_2\text{O}_3 + \text{BO}_2^{2-} + 0.5\text{H}_2\text{O} \rightarrow 2\text{BO}_2^{4-} + 2e^- )</td>
<td>( 2\text{BO}_2^{4-} + 2e^- )</td>
</tr>
</tbody>
</table>

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B₂O₃\cdot =2B₂O₃+0.5O₂+2e⁻ \quad (10)
SiO₃²⁻=SiO₂+0.5O₂+2e⁻ \quad (11)
SIF₆²⁻=SiF₄+F₂+2e⁻ \quad (12)
2BF₄⁻=2BF₃+F₂+2e⁻ \quad (13)

Combinations of the anodic reaction with various realizations of cathodic reduction give chemical reactions shown in tables 1 and 2.

Electrochemical circuits corresponding to these chemical reactions can be represented as follows:

Z|M₂O₅|M₂O₅⁻₀.5O₂||M₂O₅⁻₀.5O₂/M₂O₅⁻₀.5O₂, O₂, Pt, \quad (14)
M|M₂O₅|M₂O₅⁻₀.5O₂||M₂O₅⁻₀.5O₂, ZO₅/₂, Pt, \quad (15)
Si|K₂SiF₆, KF||K₂SiF₆, SiF₄|F₂, Pt, \quad (16)
B|K₂BF₄, KF||K₂BF₄, BF₃|F₂, Pt, \quad (17)
Z|ZO₅/₂|O₂, Pt, \quad (18)
where Z=B, Si; M=Na, K, Li; z-valence of Z.

From values of decomposition voltage, it follows that process of immediate deposition of boron and silicon should be energetically more favorable. However, which reaction will really occur, will depend on the kinetic characteristics of the processes.

Table 1 and 2 show the values of the equilibrium potentials of deposition of boron and silicon from their oxide and halide compounds calculated from the EMF of cells (14) and (18).

**Table 1**

<table>
<thead>
<tr>
<th>Decomposition reaction</th>
<th>298</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂O₇=SiO₂+O₂</td>
<td>2.202</td>
<td>1.928</td>
<td>1.882</td>
<td>1.836</td>
<td>1.794</td>
</tr>
<tr>
<td>Li₂SiO₅=Si+Li₂O₅+O₂</td>
<td>2.353</td>
<td>2.275</td>
<td>2.231</td>
<td>2.189</td>
<td>2.148</td>
</tr>
<tr>
<td>Li₂SiO₃O₇=2Si+Li₂O₅+2O₂</td>
<td>2.341</td>
<td>2.093</td>
<td>2.053</td>
<td>2.025</td>
<td>1.986</td>
</tr>
<tr>
<td>Mg₂SiO₅=Si+MgO+O₂</td>
<td>2.384</td>
<td>2.040</td>
<td>2.034</td>
<td>1.988</td>
<td>1.945</td>
</tr>
<tr>
<td>Mg₂SiO₅O₅=Si+2MO₂+O₂</td>
<td>2.585</td>
<td>2.272</td>
<td>2.227</td>
<td>2.169</td>
<td>2.131</td>
</tr>
<tr>
<td>Na₂SiO₃O₇=Na₂SiO₆+O₂</td>
<td>2.716</td>
<td>2.466</td>
<td>2.447</td>
<td>2.406</td>
<td>2.373</td>
</tr>
<tr>
<td>Na₂SiO₅O₇=2Si+Na₂O₆+2O₂</td>
<td>2.475</td>
<td>2.233</td>
<td>2.193</td>
<td>2.153</td>
<td>2.114</td>
</tr>
<tr>
<td>Si₂K₆F₁₄=Si₂+2K₂F₂</td>
<td>4.074</td>
<td>3.848</td>
<td>3.810</td>
<td>3.773</td>
<td>3.736</td>
</tr>
<tr>
<td>K₂BF₄=BF₃+2F₂</td>
<td>5.855</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Na₂SiF₆=Si+2NaF₂</td>
<td>5.830</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Decomposition reaction</th>
<th>298</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>4LiBO₂O₇=2Li₂O₅+4B+3O₂</td>
<td>2.371</td>
<td>2.120</td>
<td>2.081</td>
<td>2.047</td>
<td>2.005</td>
</tr>
<tr>
<td>4NaBO₂O₇=4B+4Na₂O₅+3O₂</td>
<td>2.547</td>
<td>2.272</td>
<td>2.235</td>
<td>2.190</td>
<td>2.148</td>
</tr>
<tr>
<td>2B₂O₅=4B+3O₅</td>
<td>2.018</td>
<td>1.793</td>
<td>1.755</td>
<td>1.717</td>
<td>1.679</td>
</tr>
<tr>
<td>Na₂E₂O₅=4B+Na₂O₅+3O₂</td>
<td>2.533</td>
<td>2.068</td>
<td>2.025</td>
<td>1.980</td>
<td>1.937</td>
</tr>
<tr>
<td>2Na₂B₂O₇=6B+2Na₂+Na₂BO₂⁺+4O₂</td>
<td>2.215</td>
<td>1.941</td>
<td>1.895</td>
<td>1.852</td>
<td>1.805</td>
</tr>
<tr>
<td>2Na₂B₂O₃=3B+Na₂+Na₂O₇</td>
<td>2.268</td>
<td>1.976</td>
<td>1.930</td>
<td>1.886</td>
<td>1.841</td>
</tr>
<tr>
<td>Na₂E₂O₇=2B₂O₅+2Na₂O+3O₂</td>
<td>3.045</td>
<td>3.073</td>
<td>2.986</td>
<td>2.908</td>
<td>2.806</td>
</tr>
<tr>
<td>2Na₂SiO₅=4B+Na₂BO₂⁺+3O₂</td>
<td>2.139</td>
<td>1.857</td>
<td>1.815</td>
<td>1.771</td>
<td>1.726</td>
</tr>
<tr>
<td>Li₂B₂O₇=2Li₂O₅+3O₂</td>
<td>2.272</td>
<td>1.976</td>
<td>1.938</td>
<td>1.899</td>
<td>1.856</td>
</tr>
<tr>
<td>2Li₂B₂O₇=4B+4LiBO₂⁺+3O₂</td>
<td>2.115</td>
<td>1.843</td>
<td>1.795</td>
<td>1.751</td>
<td>1.707</td>
</tr>
<tr>
<td>K₂B₂O₇=4B+K₂O₇+5O₂</td>
<td>2.389</td>
<td>2.113</td>
<td>2.090</td>
<td>2.049</td>
<td>2.009</td>
</tr>
<tr>
<td>2KB₂O₇=2B₂+2K₂O₇+3F₂</td>
<td>4.333</td>
<td>3.851</td>
<td>3.782</td>
<td>3.714</td>
<td>3.659</td>
</tr>
<tr>
<td>2NaBF₄=2B+NaF₂+3F₂</td>
<td>4.111</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2BC₂O₇=2B+3Cl₂</td>
<td>1.340</td>
<td>1.235</td>
<td>1.218</td>
<td>1.200</td>
<td>1.182</td>
</tr>
<tr>
<td>2EF₃=2B+3F₂</td>
<td>3.865</td>
<td>3.739</td>
<td>3.718</td>
<td>3.695</td>
<td>3.673</td>
</tr>
</tbody>
</table>
Oxyhalides, halides, and oxo-salts of alkali and alkaline earth metals have been calculated by us previously [5,8,10].

From the results of calculations (Table 3), it can be seen that the deposition potentials for Cr, Mo, and W metals and silicon (boron) are significantly different. Therefore, unlike electrosynthesis of Cr, Mo, and W metal carbides, electrochemical synthesis at high temperature of their silicides and borides is possible only in a kinetic mode.

Synthesis in this case occurs in such a manner that more electronegative component is deposited onto more electropositive component with subsequent chemical reaction. This variant of the synthesis takes place in the reaction diffusion mode; therefore, in addition to the electrochemical factors, temperature and time are also determinants. Electrosynthesis will be carried out at higher temperatures compared with the synthesis occurring in thermodynamic mode, and phase composition will depend on process duration.

Thermodynamic analysis of the decomposition voltage of similar compounds of boron, silicon, chromium, tungsten, and molybdenum has shown that these metals are more electropositive than boron and silicon for 0.5-0.7 V. Values of depolarization of boron and silicon deposition onto tungsten and molybdenum are no more than 200 mV.

Therefore, the synthesis of chromium, tungsten, and molybdenum borides and silicides is possible only in the kinetic mode. To manage this kind of synthesis, one should know about peculiarities of process of electrodeposition of components forming silicide or boride. Features of electrodeposition of chromium, molybdenum, and tungsten from melts of different composition are described in detail by us in [44]. As for silicon and boron, it was necessary, using available data [45-48], to find out their electrochemical behavior in selected systems.

Systems for the synthesis were selected on the base of the results of thermodynamic analysis, and also on the base of the following considerations. Since the synthesis of Cr, Mo, and W metals borides and silicides takes place in reaction diffusion mode, it will be carried out at relatively high temperatures (above 1123 K). Halide systems are not suitable for industrial use in this case due to the high volatility and thermal instability of the components (fluorosilicates and fluoroborates). Consequently, the most suitable are oxide compounds of silicon and boron, namely SiO₂ and B₂O₃, because silicon in elementary form is hardly deposited from its oxyanion forms SiO₃²⁻ and SiO₄⁴⁻.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>COMPONENTS FOR THE ELECTROCHEMICAL SYNTHESIS OF CHROMIUM, MOLYBDENUM AND TUNGSTEN, METAL BORIDES AND SILICIDES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compounds</td>
<td>( T/K )</td>
</tr>
<tr>
<td>SiO₂-K₂CrO₄</td>
<td>298</td>
</tr>
<tr>
<td>SiO₂-Na₂MoO₄</td>
<td>298</td>
</tr>
<tr>
<td>Na₂Si₃O₇-Na₂MoO₄</td>
<td>298</td>
</tr>
<tr>
<td>SiO₂-Na₂WO₄</td>
<td>900</td>
</tr>
<tr>
<td>Na₂Si₃O₇-Na₂WO₄</td>
<td>900</td>
</tr>
<tr>
<td>B₂O₃-Na₂CrO₄</td>
<td>298</td>
</tr>
<tr>
<td>B₂O₃-Na₂MoO₄</td>
<td>298</td>
</tr>
<tr>
<td>B₂O₃-Na₂W₂O₄</td>
<td>900</td>
</tr>
</tbody>
</table>

Fig. 2 Cyclic voltammograms obtained at \( T=1173 \) K with \( 0.1 \) V·s⁻¹ polarization rate for NaCl (1) and NaCl with different additions of Na₃AlF₆ (2,3,4); cathode was Pt (1,2) and glassy carbon-GC (3,4).

Fig. 3 Cyclic voltammograms obtained on the melts of NaCl-Na₃AlF₆ (a,c) and on NaCl-Na₃AlF₆ with different additions of SiO₂ (b,d); \( T=1173 \) K, polarization rate \( 0.1 \) V·s⁻¹.
The use of melts of alkali metal fluorides as solvents for SiO2 and B2O3 is also not possible since these salts convert SiO2 and B2O3 to higher fluorides.

It seems to us that the most suitable solvent for oxides of silicon and boron can be NaCl-Na3AlF6 melt, because, unlike the alkali metal fluorides the fluoride ion is bound here to a stable complex [AlF6]3-. Oxides of silicon and boron in this melt are stable and dissolve in a sufficient amount of it. Furthermore, this system, as shown in [39], is suitable for electrodeposition of chromium, molybdenum, and tungsten.

**Theoretical backgrounds of ESMS**

Electroreduction of Si (IV) and B (III) against the molten NaCl-Na3AlF6 (1:1 molar ratio)

The most detailed studies of processes of electrochemical reduction of silicon dioxide in molten cryolite are published in literature [44,45]. The measurement of potential versus time in Na3AlF6-SiO2 melt [45] has shown that the electroreduction at a nickel cathode includes a weak predissociation of complex to the active state followed by four-electron process of Si4+ discharge:

\[
\text{SiO}_2 \rightarrow \text{Si}^{4+} + 2\text{O}^2- \quad (19)
\]

\[
\text{Si}^{4+} + 4e^- \rightarrow \text{Si} \quad (20)
\]

The authors of [44] have measured potential versus time for Na3AlF6-AlF3-Al2O3-SiO2 melt using platinum cathode at 1173 K. The presence of several waves on the E(t) curves enabled the authors to conclude that the electroreduction of Si (IV) has several stages with intermediate formation of compounds with silicon in lower oxidation degree.

It is known that silicon and aluminum are fairly active elements to form various alloys with platinum. When using platinum as the cathode for electrochemical measurements in these systems, the main process can be overlapped by alloy formation processes, so the interpretation of measurement results is difficult. In addition, a focused selection of components for electrochemical synthesis is not possible without knowledge of the potentials of silicon deposition. Presented in [44] potentials of silicon deposition are significantly different from those calculated by us using thermodynamic values (see above). Therefore, we have attempted to search indifferent material, and to obtain new information on the electrochemical behavior of Si (IV) in NaCl-Na3AlF6 melt with its help. Figure 2 shows the current-voltage dependences of the molten sodium chloride with sequential addition of cryolite.

Small additions of Na3AlF6 (less than 1.0 wt.%) lead to the appearance of three waves at the potentials -1.2, -1.5, and -1.7 V. At higher concentrations of cryolite, fourth wave appears at a potential -2.0 V. These data suggest that the platinum electrode is indifferent only above -1.2 V. The observed waves are associated with the processes of the alloy formation and of the immediate deposition of aluminum from AlF63-. Quite a different picture is observed during the polarization of the GC cathode (Fig. 3c). In this case, the region of potentials at which the electrode is indifferent in the NaCl-Na3AlF6 system is expanding significantly. Isolation of SiO2 reduction wave at a platinum cathode is not possible. However, at GC cathode, well-reproducible wave of electroreduction of silicon (IV) is observed which potential is close to the thermodynamic potential of silica decomposition. Potentiostatic electrolysis at this potential gives the cathode deposit consisting of free silicon.

Figure 4 shows the volt-ampere dependences for NaCl-Na3AlF6 (1:1 molar ratio) melt with sequential addition of SiO2. Reduction wave appears at a potential -1.6 — -1.9 V and is characterized by the following features: the wave is stretched along the potential axis; limiting current is not clearly expressed; on the reverse dependences \(i(E)\), two peaks of dissolution of the cathodic cycle product are found. At SiO2 concentration less than 1 wt.%, limiting current increases in direct proportion to the concentration of SiO2 (fig. 5). On this basis, one can conclude that the SiO2 solubility in molten NaCl-Na3AlF6 (1:1) is about 1.0 wt.%. It can be assumed that the dissolution of SiO2 in the NaCl-Na3AlF6, as in pure cryolite [41,45-47], is connected with complex oxyfluorides formation.

Analysis of the current-voltage relationships in a semilogarithmic coordinate system \(\lg[i/(i_d-i)] = f(E)\) shows that the slope of the experimental lines described by dependences \(i(E)\) is 0.087-0.108. It is more than for four-
The electrochemical behavior of the molten NaCl-NaAlF₆ melt as a solvent for boron oxide. The electrochemical behavior of boron against this melt has not been studied previously. Therefore, to realize the electrosynthesis of VI-B group metals borides, it was necessary to find out peculiarities of the electrochemical behavior of boron against the cryolite-chloride melt.

Figure 6 presents volt-ampere dependences for NaCl-NaAlF₆ melt with sequential addition of boron oxide. Small additions of boron oxide lead to the appearance of reduction wave at a potential -1.5 — -1.9 V versus platinum-oxygen electrode. The height of the wave increases with increasing concentration of B₂O₃ in the melt; however, it is not possible to establish a quantitative relationship.

Waves are extended along the potential axis. Appearance of the cyclic voltammograms indicates irreversible nature of the charge transfer step. Moreover, with boron oxide concentration increase, the irreversibility degree of the process is also increasing. Product of potentiostatic electrolysis at potential -1.7 — -1.9 V is dispersing powder of amorphous boron. We did not attempt to determine the detailed mechanism of electroreduction of B₂O₃. Based on the current-voltage measurements data, process of electroreduction can be schematically represented as follows:

\[
\text{B}_2\text{O}_3 + \text{AlF}_6^2- \rightarrow 2\text{BOF} + \text{AlOF} + 3\text{F}^- \quad (22)
\]

\[
\text{BOF} + 3e^- \rightarrow \text{B} + \text{O}_2^- + \text{F}^- \quad (23)
\]

The electrochemical behavior of the molten NaCl-NaAlF₆ system under the joint presence of tungstate (molybdate, chromate) of sodium and silicon oxide (boron oxide) comparison of potentials of electrodeposition of tungsten and molybdenum from chloride-cryolite melt containing sodium tungstate and molybdate with potentials of kinetic mode, led us to consider the use of NaCl-NaAlF₆ melt as a solvent for boron oxide. The electrochemical behavior of boron against this melt has not been studied previously. Therefore, to realize the electrosynthesis of VI-B group metals borides, it was necessary to find out peculiarities of the electrochemical behavior of boron against the cryolite-chloride melt.

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\]
measurements have shown that the electrosynthesis of tungsten silicides from molten salts. Electrochemical synthesis of powders of molybdenum and chromium, molybdenum and tungsten silicides and borides will occur in the kinetic mode. Data confirm once again that the electrosynthesis of metals oxyfluoride complexes, tungsten, molybdenum, electrolysis at potentials of electroreduction of refractory difference is the fact that, during the potentiostatic higher than that of tungsten, respectively. One more potential of electroreduction of oxyfluoride complexes of metal tungsten [39], the reaction diffusion of silicon or boron into the metal-salt aggregate with formation of silicide and boride phases of different composition up to the higher borides and silicides Msi and MBx.

The duration of the first stage of the synthesis depends on the amount of refractory metal in the system and on the cathode current density. To obtain tungsten or molybdenum in the form of fine powder, the current density should be maximized. The second stage begins with the deposition of the electropositive component.

Synthesis of borides or silicides was realized only under the condition that the powders of tungsten or molybdenum are deposited on the cathode as a metal-salt aggregate of such size and shape that allow it to be persistent on the cathode without destruction. In case of scaling of metal (Mo or W) powders down to the bottom of the electrolyzer, components are not in contact, and the synthesis does not occur.

By the traditional way, borides and silicides of tungsten and molybdenum was prepared at the 1373-1673 K; and electrosynthesis at 1123-1273 K. The energy gain (and, therefore, the reduction of synthesis temperature) is provided by interaction of fine powders of tungsten, molybdenum, silicon, or boron deposited at the cathode.

Optimization of the process of electrosynthesis of borides and silicides consisted in determination of the concentration ratios, current densities, temperatures, duration of the process etc. The process of obtaining of borides and silicides can be described by the following electrochemical and chemical equations:

- at the cathode:
  \[ \text{MO}_2F_4 \rightarrow \text{M} + 2\text{O}^2- + 4\text{F}^- \]  
  \[ \text{SiO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Si} + \text{H}_2\text{O} \]  
  \[ \text{B}_2\text{O}_3 + 3\text{H}^+ + 3\text{e}^- \rightarrow 2\text{B} + 3\text{H}_2 \]  

- at the anode:
  \[ 3\text{Na}_2\text{CO}_3 + \text{O}_2 \rightarrow 2\text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{O}_2 \]  
  \[ 2\text{Na}_2\text{O} + \text{SiO}_2 + 6\text{e}^- \rightarrow 2\text{Na}_2\text{SiO}_3 \]  

Electrosynthesis of silicides of molybdenum and tungsten was carried out in the molten mixture NaCl-NaAlF₄-Na₂Mo₄O₁⁶-SiO₂ (M = Mo, W). Selecting the concentration ratios of components guided by the following considerations: according to [46, 47], silica has limited solubility (8.82 wt.% at 1283 K) in the cryolite melt. The addition of sodium chloride to cryolite reduces the melting point of the mixture and the solubility of SiO₂. In the eutectic melt containing 68.5 wt.% NaCl and 31.5 wt.% Na₂AlF₆ (T=1010 K), the solubility of silica is 1.0 wt.%. The maximum content of molten cryolite in binary system NaCl-NaAlF₄ allowing to carry out electrolysis at 1173 K is 70 wt.%. The solubility of SiO₂ in the melt of such composition is approximately 2.0 wt.%.

Therefore, in the selected area of the binary NaCl-NaAlF₄ system (from eutectic up to 70 wt.% of Na₂AlF₄), SiO₂ solubility determines the necessary concentration of sodium tungstate (molybdate) to obtain silicides of stoichiometric composition. Melt components concentration range, wt.%: NaCl:29.0-67.5, Na₂AlF₆:31.0-67.0, Na₂Mo₄O₁⁶:0.5-2.0, SiO₂:1.0-2.0. With the NaCl...
concentration more than 67.5 wt.%, SiO₂ solubility in the melt is less than 1.0 wt.%. Thus, the concentration of Na₂MoO₄ for the silicides MoSi₂ and WSi₂, formation should be less than 0.5 wt.%, i.e. the process becomes inefficient. If the Na₂AlF₆ concentration is more than 67.0 wt.%, the melt is liquefied above 1173 K and the synthesis should be carried out at a temperature above 1223 K with decrease of metal salt aggregate stability when temperature raise. Furthermore, the higher the cryolite content in melt is, the more complicated cleaning process of synthesis product is to be used, and the more aggressive and less practical melt becomes.

Choosing concentration of oxosalts of refractory metal, first stage of electrosynthesis must be taken into account. The first stage is formation of metal-salt aggregate, and the deposition of silicon begins with the deposition of oxosalt of refractory metal. Therefore, the higher the oxosalt concentration is, the longer time (with i=const) is necessary for formation of metal-salt aggregate. This metal-salt aggregate grows large. Accordingly, the ability of sediment to be hold at the cathode (the stability of the aggregate) decreases, and complete conversion of the deposited molybdenum and tungsten into silicides is not achieved.

Therefore, with Na₂MoO₄ content in the melt over 2.0 wt.%, free tungsten and molybdenum are present in the final product. If the concentration of Na₂MoO₄ is less than 0.5 wt.%, free silicon appears in the final product. At even lower Na₂MoO₄ concentrations, silicon-aluminum alloys are obtained. Temperature and current density are essential for electrosynthesis. At temperatures below 1123 K, the completeness of interaction between Mo (W) and Si is not achieved. At temperatures above 1223 K, metal-salt aggregate stability decreases, and silicides are not formed.

At the optimum composition of the melt, pure silicides MoSi₂ (WSi₂) are obtained with the current density 0.5-1.2 A·cm⁻² for MoSi₂, and 0.5-1.5 A·cm⁻² for WSi₂. With the current density below 0.5 A·cm⁻², the desired product is contaminated by free molybdenum or tungsten. With the current density above 1.2 A·cm⁻², double silicide Mo(Al, Si)₂ phase appears in molypdate containing melt. In tungsten containing melts, with the current density above 1.5 A·cm⁻², silicon-aluminum alloy is obtained in addition to WSi₂. Within the range 0.5-1.5 A·cm⁻², with an increase of the current density, specific surface area of obtained silicides of molybdenum and tungsten is also increased (Sₚ =5-15 m²·g⁻¹).

Using Tesla BS-300 scanning electron microscope, the shape and size of the MoSi₂ powder particles were studied. These particles are characterized by presence of weakly adherent conglomerates with average size 0.5-2.0 microns. Since the silicides are formed in the reaction diffusion mode, the duration of the process must substantially influence the composition of the products obtained. The data presented in table 4 show the dependence of the phase composition of the cathode deposits on the electrolysis time for electrolytes of the optimum composition, temperature, and current density.

<table>
<thead>
<tr>
<th>Time/min</th>
<th>Current density/A·cm⁻²</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.0</td>
<td>Mo₂Si₂, MoSi₂</td>
</tr>
<tr>
<td>20</td>
<td>1.0</td>
<td>Mo₂Si₂, MoSi₂</td>
</tr>
<tr>
<td>30</td>
<td>1.0</td>
<td>Mo₂Si₂, WSi₂</td>
</tr>
<tr>
<td>45</td>
<td>1.0</td>
<td>Mo₂Si₂</td>
</tr>
<tr>
<td>60</td>
<td>1.0</td>
<td>Mo₂Si₂, Si</td>
</tr>
</tbody>
</table>

Electrochemical synthesis of molybdenum and tungsten borides

Electrochemical synthesis of tungsten and molybdenum borides was carried out in the molten NaCl-Na₂AlF₆-Na₂MoO₄-B₂O₃-Na₂B₄O₇ mixture. In these systems, depending on the composition and parameters of electrolysis, both individual phases of refractory metal and its higher boride MB₅, and mixtures of these phases including MB, MB₅, MB₆. Optimization of the process of borides electrosynthesis lies in determination of the mode of obtaining of higher boride MB₅, having the most valuable physical and mechanical properties. As in the case of the silicides synthesis, the molten NaCl-Na₂AlF₆ (1:1 molar ratio) mixture was used as solvent for oxides.
and oxosalts of refractory metal and boron. Unlike SiO₂, boron oxide and borax are readily soluble in the molten mixture. Choosing a concentration of oxide and oxosalt of refractory metal, it is necessary to take into account the first stage of electrosynthesis, when the deposition of tungsten and molybdenum takes place to form the metal-salt deposit. Boron deposition begins as oxide and oxosalt of refractory metal form. The optimum concentration of the oxide and oxosalt of refractory metal is 0.75-1.5 wt.% At higher concentrations, due to the instability of metal-salt aggregate, complete boriding of deposited refractory metal are not achieved. We have investigated the effect of the concentration of boron oxide and borax on the composition of cathodic deposits. The appearance of boride phase in the cathode deposit begins with the content of boron oxide or borax in the melt 5 wt.%. With increase of the concentration of boron oxide (borax), the amount of boride phases in the cathode deposit increases. Within the range of B₂O₃ and Na₂B₄O₇ concentrations 10-20 wt.%, complete boriding of refractory metal with formation of higher boride phase MoB₄ or WB₄.

Of great significance during the electrosynthesis of borides, the temperature is. With T<1073 K, complete interaction between Mo (W) and B is not achieved. Above 1223 K, stability of metal-salt aggregate decreases and borides are not formed. Electrosynthesis of molybdenum and tungsten borides were carried out in potentio- and galvanostatic modes. It turned out that these modes are not equal for this process. In the galvanostatic mode, the true current density value is known only in the initial period since cathode surface area changes substantially during the electrolysis. In most cases, potentiostatic mode was used since it is the voltage (potential) which determines the course of the reactions and controls the nature of the deposition reaction. If the anode material is graphite, and the cell voltage U is <2.5 V, the cathode deposit is composed mainly of metallic tungsten or molybdenum. Provided U=2.5-3.5 V, the mixture of different phases of M, M₂B, MB, and M₂B₅ is formed. If U=3.5-4.5 V, the cathode deposit consists of higher boride MB₄.

Table 6

<table>
<thead>
<tr>
<th>Current density/A cm⁻²</th>
<th>Composition</th>
<th>Specific surface area/m² g⁻¹</th>
</tr>
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<tbody>
<tr>
<td>1.2</td>
<td>MoSi₂</td>
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</tr>
<tr>
<td></td>
<td>traces of Mo(AlSi₃)</td>
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<tr>
<td>1.3</td>
<td>Mo(AlSi₃)ₓ</td>
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<tr>
<td></td>
<td>traces of MoSi₅</td>
<td></td>
</tr>
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<td>Mo(AlSi₃)ₓ</td>
<td>14.3</td>
</tr>
<tr>
<td>2.0</td>
<td>Mo(AlSi₃)ₓ</td>
<td>15.2</td>
</tr>
<tr>
<td>2.5</td>
<td>Mo(AlSi₃)ₓ</td>
<td>siliusina</td>
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</table>

Table 7

<table>
<thead>
<tr>
<th>Time(min)</th>
<th>Tension/V</th>
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</thead>
<tbody>
<tr>
<td>5</td>
<td>4.0</td>
<td>W</td>
</tr>
<tr>
<td>10</td>
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</tr>
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<td>4.0</td>
<td>W, WB, WB₅, WB₆</td>
</tr>
<tr>
<td>30</td>
<td>4.0</td>
<td>WB₅, WB₆, WB₇</td>
</tr>
<tr>
<td>45</td>
<td>4.0</td>
<td>WB₇</td>
</tr>
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</table>

Table 8

<table>
<thead>
<tr>
<th>C/ wt.%</th>
<th>min</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>30</th>
<th>45</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>Mo</td>
<td>Mo</td>
<td>Mo</td>
<td>MoB₂</td>
<td>Mo₂B₃</td>
<td>Mo₂B₄</td>
<td>Mo₂B₅</td>
</tr>
<tr>
<td>1.0</td>
<td>Mo</td>
<td>Mo₂B</td>
<td>Mo₂B</td>
<td>Mo₂B₂</td>
<td>Mo₂B₃</td>
<td>Mo₂B₄</td>
<td>Mo₂B₅</td>
</tr>
<tr>
<td>0.75</td>
<td>Mo</td>
<td>Mo₂B</td>
<td>Mo₂B</td>
<td>Mo₂B₂</td>
<td>Mo₂B₃</td>
<td>Mo₂B₄</td>
<td>Mo₂B₅</td>
</tr>
<tr>
<td>0.50</td>
<td>Mo</td>
<td>Mo₂B</td>
<td>Mo₂B</td>
<td>Mo₂B₂</td>
<td>Mo₂B₃</td>
<td>Mo₂B₄</td>
<td>Mo₂B₅</td>
</tr>
</tbody>
</table>

Similar dependence of the deposit phase composition on the electrolysis time is observed in the NaCl-Na₃AlF₆-Na₂MoO₄-B₂O₃ system (table 8). The optimal duration of electrolysis to produce MB phases is 45-60 min. Generally, the process of electrosynthesis of molybdenum and tungsten borides is determined by the following interrelated parameters: the composition of the electrolyte, the cell voltage, the duration of electrolysis, and the temperature. The optimum values of these parameters are as follows: the composition of the melt (wt.%): NaCl:39-44.5, Na₃AlF₆:39.25-44.5, Na₂MoO₄ (MoO₃):1-1.5, Na₂B₄O₇.
The formation of higher silicide CrSi occurs through the stages of formation of lower silicides. In the high-temperature electrochemical synthesis conditions (973-1173 K) most thermodynamically favorable process is CrSi and CrSi, silicides formation and oxidation of Si to SiO2. Experimental data (table 9) show that the process of silicon thermic reduction of CrO3 depends on several factors, among which, a crucial role is played by the temperature and process duration.

At the current-voltage dependences of the joint electroreduction in molten NaCl-NaAlF4-K2CrO4-B2O3 systems, reduction waves are observed at significantly different potentials: -0.7 — -0.9 and -1.4 — -1.7 V, respectively. At the first stage of the electrochemical synthesis, chromium is deposited in the form of CrO3, interacting with the boron deposited during the second stage of electrolysis to form borides. Electrochemical synthesis of chromium borides was carried out in molten NaCl-NaAlF4-K2CrO4-B2O3 mixture. Depending on the composition of the melt and electrolysis parameters, both individual phases CrO3, CrB, CrB, CrB, and mixtures thereof were obtained (table 11). The yield of single-phase product CrB was 0.14-0.21 g/A-h. Fine powders have specific surface area 10-20 m2·g-1. Thermodynamic calculations for boron thermic reduction of CrO3 were not performed as reference data for chromium borides are missing.

Generally, the process of chromium borides high-temperature electrochemical synthesis is determined by the following interrelated parameters: the composition of the electrolyte, the cell voltage, temperature, and the duration of electrolysis. The optimum composition of the melt is as follows, wt.%: NaCl: 39-44.5, NaAlF4: 39-44.5, K2CrO4: 1-1.5, B2O3: 10-20.0. The optimal parameters of electrolysis are following: the cell voltage 3.5-4.5 V, the temperature 1173-1223 K, duration of electrolysis 45-60 min, current density 1.0-1.8 A/cm2.

Chemical analysis of the electrolyte after the electrolysis has shown that the chromium is removed virtually completely from the melt. To carry out the electrolysis process further, the addition of the refractory metal oxide or oxosalts is required.

Conclusions
We systematized the well-known electrolytes for the high-temperature electrochemical synthesis of powders of silicides and borides compounds of chromium, molybdenum and tungsten metals, according to the classes of synthesized compounds. We also described the results
of recent investigations into the ionic melts electrochemical synthesis.

Acknowledgement: This work was conducted with the financial support of a bilateral project Romanian-Ukraine (Romanian Ministry of Education and Science, Capacities Programm -PN2 no.203/28.03.2009. Authors equally contributed to this work.

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Table 11
THE DEPENDENCE OF PRODUCT COMPOSITION ON CHROMATE CONCENTRATION AND ELECTROLYSIS TIME FROM NaCl-NaAlF4-B2O3-(10 wt.%)K2CrO4 SYSTEM AT T=1173 K, U=3.5 V

<table>
<thead>
<tr>
<th>Cwt%</th>
<th>t(min)</th>
</tr>
</thead>
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